

Final Report.

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“Retrieval of Atmospheric CO₂ Column from Ground-based Near IR Spectra of the Sun”

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This grant has supported a graduate research assistant stipend for Zhonghua Yang, a geochemistry Ph.D. student at Caltech. In this project, we have significantly improved the retrieval of atmospheric column CO₂ (and molecular oxygen) from ground-based, high resolution near-IR solar transmission spectra. This work has greatly benefited from interactions with Dr. Geoffrey Toon and Stan Sander of NASA's Jet Propulsion Laboratory and with James T. Randerson, University of California - Irvine.

The results from this study are summarized in three publications, reprints of which are enclosed with this report:

1. Atmospheric CO₂ retrieved from ground-based near IR solar spectra, Z. Yang, G. C. Toon, J. S. Margolis, and P. O. Wennberg, *Geophys. Res. Lett.*, **29**, doi: 10.1029/2001GL014537, 2002.
2. Ground-based photon path measurements from solar absorption spectra of the O₂ A-band, Z. Yang, P.O. Wennberg, R.P. Cageao, T.J. Pongetti, G.C. Toon, S.P. Sander, *J. Quant. Spec. Radiative Trans.*, **90**, 309–321, 2005.
3. Seasonal and latitudinal variations of column averaged volume-mixing ratios of atmospheric CO₂ T. Warneke, Z. Yang, S. Olsen, S. Korner, J. Notholt, G. C. Toon, V. Velazco, A. Schulz, and O. Schrems, *Geophys. Res. Lett.*, **32**, doi:10.1029/2004GL021597, 2005.

In paper 1., we demonstrated that the vertical column averaged atmospheric carbon dioxide dry mole mixing ratio (here after XCO₂) could be determined with a precision of better than 0.5% from archived solar spectra obtained from Kitt Peak. This result was a substantial improvement on earlier efforts to analyze the same spectra (Wallace and Livingston, *J. Geophys. Res.*, **95**, 9823, 1990). The results of this study were used by the OCO science team to propose that ground-based FTS observations will form the basis of the validation of future satellite observations of the CO₂ column. This study also formed the basis of an ongoing effort to create a network of FTS instruments for greenhouse column gas measurements that is currently being implemented with support from NASA and our European, Australian, and New Zealand colleagues.

In paper 2, we demonstrated that oxygen measurements in the near-IR could produce precise airmass estimates. In this study we analyzed spectra obtained by Stan Sander and colleagues at JPL of the so-called oxygen A-band. This transition is used extensively in the cloud-physics community to measure photon path in cloud. In our study, we showed, however, that the current spectroscopy of this band is insufficient to yield good estimates of the

photon path. In particular, the lineshapes are considerably broader than expected. We point to the need for better laboratory measurements of the pressure-broadened lineshapes. In response to our paper, several efforts are now underway to investigate this spectroscopy in the laboratory.

In paper 3, column observations from Justus Nolltholt's group (Bremen, Germany) have been analyzed and compared with model estimates for the annual and hemispheric variability of XCO_2 . These observations are currently being used to test early retrievals of XCO_2 from Sciamachy (Buchwitz *et al.*, *Atmos. Chem. Phys.*, **5**, 941–962, 2005).

Finally, Zhonghua Yang has aided significantly in the development and operation of the first dedicated near-IR FTS that was assembled at Caltech and deployed to Park Falls, Wisconsin. This instrument, developed with separate funding from NASA serves as the design breadboard for further instruments currently being assembled by the OCO project. The first year of data from Park Falls is shown the figure 1.

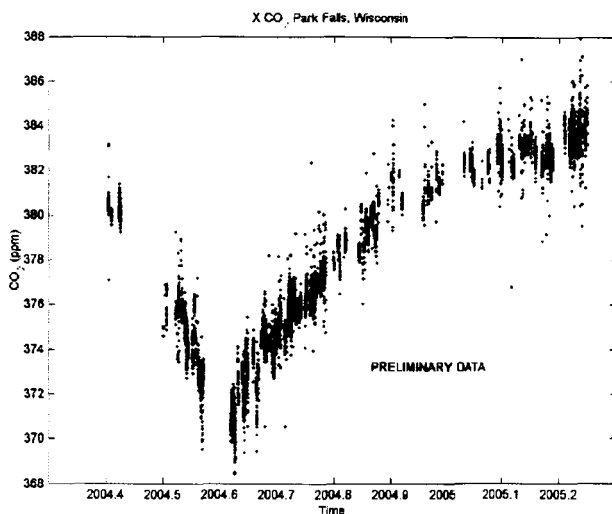


Figure 1. The column averaged dry mole mixing ratio of carbon dioxide (XCO_2) as measured at Caltech with a new FTS instrument. Precision is of order 0.2% and accuracy is estimated to be better than 1% from intercomparison with column CO_2 determined from integration of aircraft in situ profiles (Washenfelter *et al.*, in preparation).